Investigations into the synthesis of phenaliporphyrins

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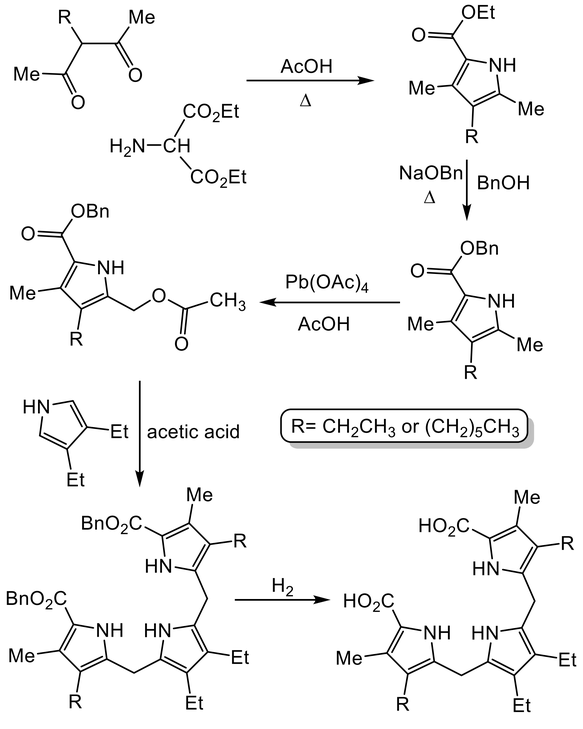
Abstract

Benziporphyrins are nonaromatic porphyrinoids with a cross-conjugated 6π electron arene subunit. However, modification of this system can result in the formation of aromatic macrocycles. In this project, a benziporphyrin-like system incorporating a phenalene subunit has been targeted for investigation. It is anticipated that this porphyrinoid will take on fully aromatic characteristics while retaining a fused naphthalene moiety. The required precursors to the phenaliporphyrin are alkyl substituted tripyrranes, and the tricyclic dialdehyde shown in Scheme 6. Initial attempts to prepare the dialdehyde by performing a Wittig condensation with perinaphthenone, followed by a Vilsmeier formylation, were unsuccessful. Currently, an alternative synthetic route to phenalidialdehyde is being developed beginning with 1-tetralone. Naphthylsuccinic anhydride has been prepared and cyclized to produce a keto acid. Subsequent esterification has been done to produce the keto ester. It is anticipated that a Wittig condensation and reduction with DIBAL-H will afford the required phenalidialdehyde. Subsequent '3+1' condensation with the tripyrranes will the afford the phenaliporphyrins.

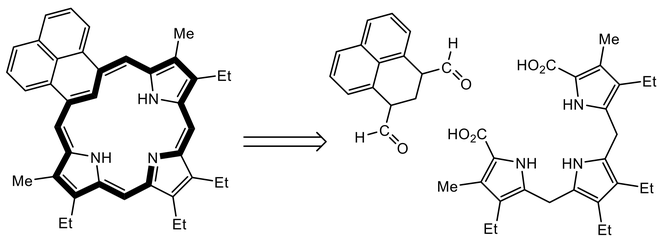
Introduction

Porphyrins are biologically active tetrapyrroles that possess 18 π-electron delocalization pathways that dominate their chemical and physical properties.[1] Carbaporphyrins are porphyrin analogues where at least one of the inner nitrogens have been replace with carbons. For example, benziporphyrin[2] is a porphyrin analogue with one of the pyrrole groups replaced by an arene unit, causing the system to become nonaromatic by being cross-conjugated. However, oxybenzi-porphyrin is aromatic due to the introduction of a keto group that enables the macrocycle to take on a porphyrin-like conjugation pathway. It has been speculated that a benziporphyrin-type structure incorporating a phenalene unit could become fully aromatic while retaining a peripheral naphthalene unit. In principle, this carbaporphyrin analogue can be synthesized by a '3 + 1' condensation by combining a tripyrrane and a phenalene dialdehyde.

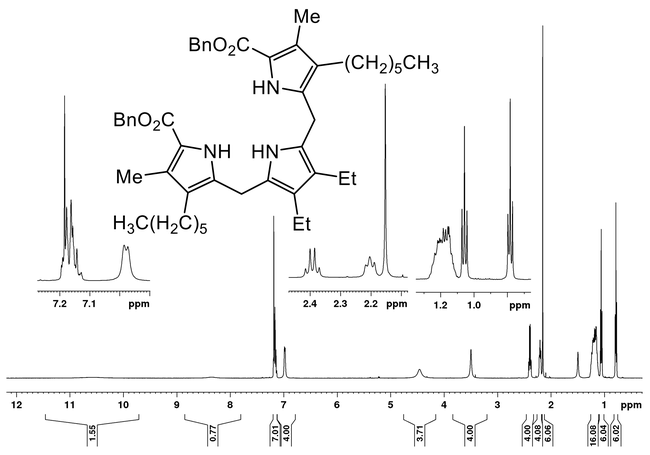
Scheme 1. Synthesis of alkyl substituted tripyrrane dicarboxylic acids



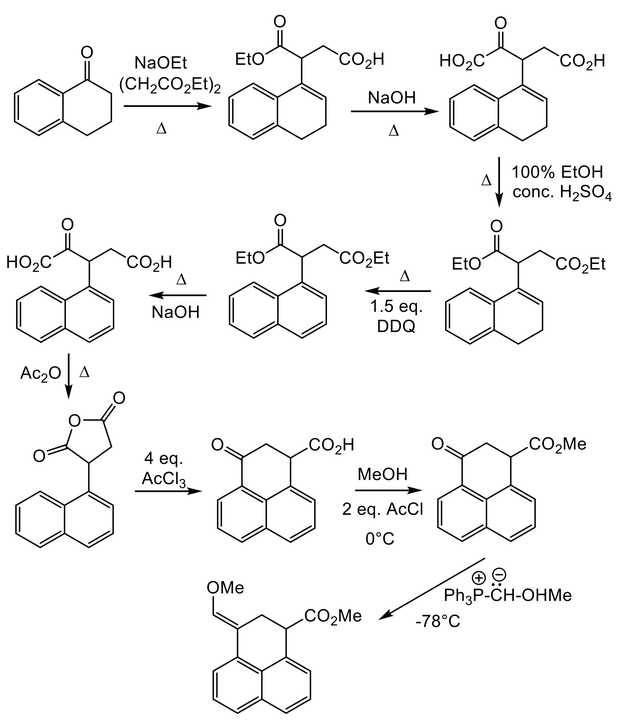
Scheme 2. Retrosynthetic analysis of phenaliporphyrin



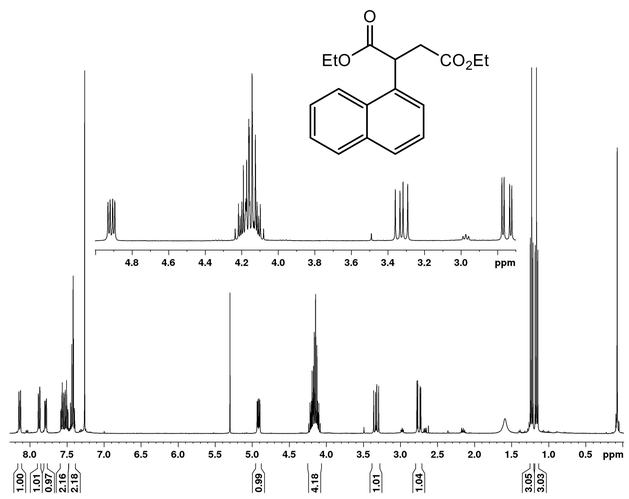
500 MHz ^{1}H NMR spectrum of hexyl substituted tripyrrane intermediate



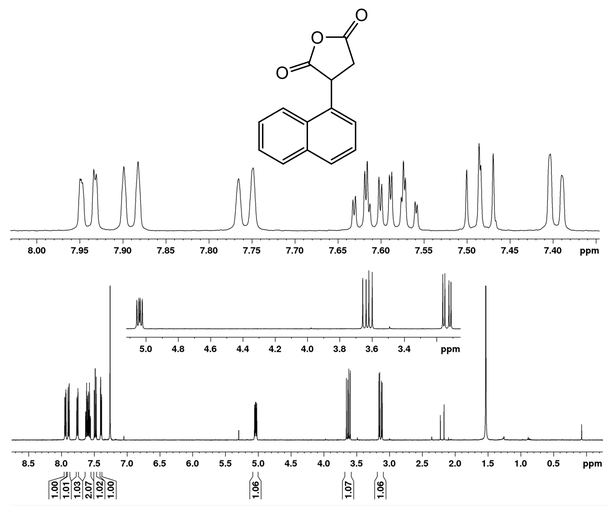
Scheme 5. Synthesis of dialdehyde precursor



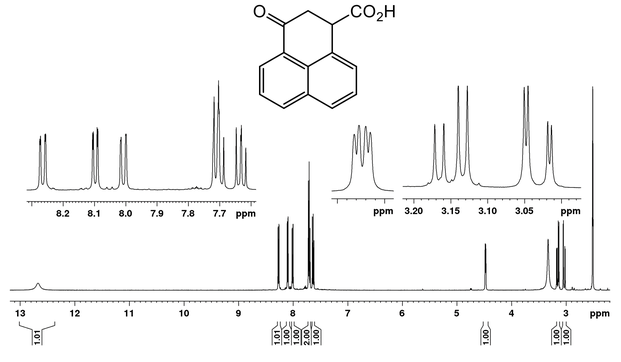
400 MHz ^{1}H NMR spectrum of oxidized diester intermediate



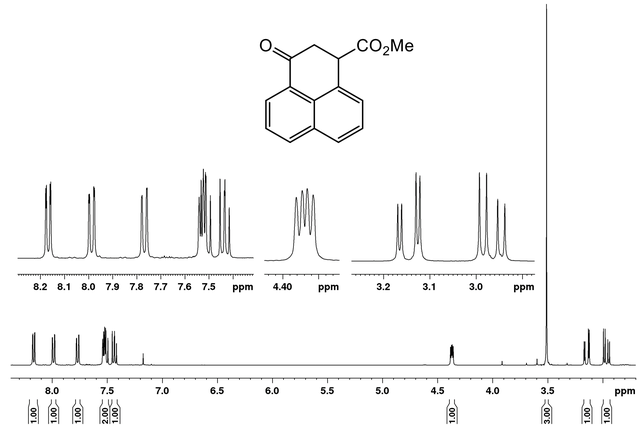
500 MHz ^{1}H NMR spectrum of naphthylsuccinic anhydride intermediate



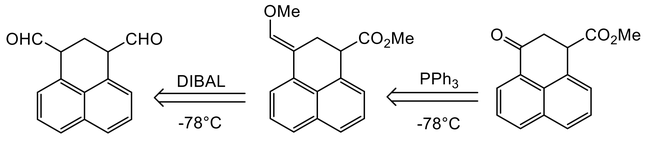
500 MHz ^{1}H NMR spectrum of keto acid intermediate



400 MHz ^{1}H NMR spectrum of keto ester intermediate



Scheme 6. Retrosynthesis of phenalidialdehyde



Conclusions

The novel aromatic porphyrinoid phenaliporphyrin has been targeted for synthesis. This requires two key intermediates, a tripyrrane and a phenalene dialdehyde. Stobbe condensation with diethyl succinate afforded a monocarboxylic acid and subsequent hydrolysis, esterification and dehydrogenation afforded diethyl 2(1-naphthyl)succinate.[3,4] Following saponification to give the corresponding dicarboxylic acid, the intermediate was cyclized with acetyl chloride to generate an anhydride. Reaction with aluminum chloride affords the keto acid intermediate.[5] Subsequent esterification with AcCl and MeOH affords the keto ester which can be converted in several steps into the required phenalene dialdehyde.[6] The hexyl and ethyl substituted tripyrranes were synthesized to investigate the solubility of the new phenaliporphyrin. The new porphyrin analogue is likely to provide insights into the nature of macrocyclic aromaticity in benziporphyrinoid systems.

References and Acknowledgments

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